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DATA SUMMARY REPORT FOR TRACE ORGANIC CONTAMINANTS IN PRECIPITATION COLLECTED AT KEJIMKUJIK NATIONAL PARK, N.S. AND ELLERSLIE, P.E.I. DURING 1983

IWD-AR-WQB-84-63

Canada

INLAND WATERS DIRECTORATE
ATLANTIC REGION
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MONCTON, N. B.

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A copy will be made available in French upon request

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ABSTRACT

A total of twenty-four wet precipitation samples were collected during 1983 and analysed for the presence of organochlorine pesticides, PCB's, chlorinated benzenes and polyaromatic hydrocarbons. Presence of α-BHC, Lindane (γ-BHC) and fluoranthene was observed in most samples, with mean concentrations of 0.016 ug/L, 0.0050 ug/L, and 0.011 ug/L, respectively. However, a relatively high annual mean concentration of PCB's (0.17 ug/L) was observed in the Ellerslie samples compared to a mean of 0.027 ug/L in Kejimkujik National Park samples. This problem encountered in previous years was attributed to one or more unknown local source. Occasional observations were also made of other contaminants present at near or below detection limit concentrations.

SOMMAIRE

Vingt-quatre échantillons de précipitations humides furent prélevés au cours de l'année 1983 et analysés pour détecter et quantifier la présence des pesticides organochlorés, des BPC (PCB's), des benzenes polychlorés, et des hydrocarbures polyaromatiques. La présence de α-BHC, de lindane (γ-BHC) et de fluoranthène fut constatés dans la plupart des échantillons avec une teneur moyenne qui est respectivement 0,016, 0,0050 et 0,011 ug/L. Toutefois une haute teneur moyenne annuelle en BPC (0,17 ug/L) fut observée dans les échantillons d'Ellerslie comparativement à une valeur moyenne de 0,027 ug/L dans les échantillons du Parc National de Kejimkujik. Ce problème, déjà rencontré lors des années précédentes, fut attribué à une ou plusieurs sources environnantes et encore inconnues. Occasionellement, la présence d'autres contaminants fut décelée à des concentrations proches ou inférieures aux seuils de détection.

INTRODUCTION

In the fall of 1980 two precipitation sample collectors were installed in the Region to study the presence of trace organic contaminants in wet precipitation. The two sites chosen were Kejimkujik National Park in Nova Scotia and the Ellerslie Fisheries Research Station in Prince Edward Island. Precipitation composite samples collected during each calendar month were analysed for organochlorinated insecticides (OC's), polychlorinated biphenyls (PCB's), chlorinated benzenes (CB's) and polyaromatic hydrocarbons (PAH's).

Results covering the period 1980 to 1982 were reported earlier in two data summary reports (1,2). The widely used insecticide lindane (γ-BHC) and one of its isomers, α-BHC, were observed in almost every sample at the low part per trillion level (ng/L). PCB's, another group of contaminants considered to be widespread in the environment were detected in the majority of samples with concentrations ranging between trace levels to a maximum of 0.18 ug/L and 0.60 ug/L in samples from Kejimkujik National Park and Ellerslie, respectively. The PCB concentrations were significantly higher at the latter site and were believed to be emanating from a local source(s). Fluoranthene, a PAH compound said to have no carcinogenic activity was also observed in the majority of samples with annual means varying between 0.010 ug/L and 0.012 ug/L. A few other OC's, CB's and PAH's were found present at very low levels but only on a sporadic basis.

This report summarizes the data obtained on twenty-four wet precipitation samples collected during 1983 at the same two sites. A

comprehensive report including data from at least five subsequent years of sampling is planned on completion of the project, probably by the end of 1985 or 1986.

SAMPLING PROCEDURE AND ANALYTICAL METHODS

Two modified Sangamo type-A precipitation collectors equipped with stainless steel buckets were used. The collectors were tended and maintained by either government or contract personnel working nearby. The sampling procedure described in (2) was followed.

The chlorinated compounds were analyzed as previously using a Varian 3700 gas chromatograph equipped with an autosampler, direct splitless injector (280°C), dual nickel-63 electron capture detectors (350°C), and a Spectra Physics model 4000 chromatography data system. A single sample injection of 1 ul was simultaneously chromatographed on two narrow-bore, high resolution fused silica columns of different polarity. The liquid phases consisted of SE-30 and SE-54, respectively. The columns measured 30 m in length by 0.25 mm I.D. and the liquid phase thickness was 0.25 micron.

The CB's were determined (3) by programming the GC oven from an initial temperature of 70°C (2 min) at a rate of 7°C/min up to a final temperature of 240°C for 45 minutes. The OC and PCB analysis involved an initial set temperature of 160°C (5 min) followed by programming at a rate of 2°C/min up to 250°C for 30 min.

The PAH's were determined by using reverse phase HPLC with fluorescence detection. The SP-8000 HPLC was equipped with a Perkin

Elmer HC-ODS-SIL-X (0.26 cm x 25 cm) 10 u column. A gradient program consisting of an acetonitrile/water mobile phase at a rate of 1.0 mL/min was used according to Reference (4). An excitation wavelength of 280 nm (7-54 filter) was selected and a cut-off filter at 370 nm was used for emission. When possible extracts were concentrated ten to twenty fold for confirmation using a fixed wavelength UV detector at 254 nm and 280 nm simultaneously.

The four groups of parameters were extracted simultaneously using 100 mL hexane per litre of water followed by a second extraction with another 100 mL hexane. When necessary fluorisil column clean-up was used to purify the sample extract before GC analysis. The hexane extract was then dried by passing it through a column packed with sodium sulfate. The eluate was evaporated to a final volume of 5.0 mL which was further divided in half for both GC and HPLC analyses, respectively.

RESULTS AND DISCUSSION

A list of the various individual compounds with corresponding NAQUADAT codes and detection limits (DL's) are given in Table 1. It should be noted that the DL's were based on sample volumes of one litre and that volumes varied constantly. This means that each sample actually had a different set of DL's. The respective DL's for the OC's and PCB's are as those specified in the NAQUADAT method description and the analytical methods manual (5). A verification of these DL's using our capillary technique gave similar results with only few exceptions. Nevertheless, for all groups of compounds the DL's were determined

in-house by repeated analysis of standard solutions at concentration levels three to five times the estimated DL's. The DL was then established as being two times the standard deviation.

Data obtained on precipitation (wet event only) collected from Kejimkujik National Park and the Ellerslie Fisheries Research Station are presented in Table 2 and Table 3, respectively. In general there appears to be nothing outstanding compared to previous data collected between 1980 and 1982. The PCB concentrations in Ellerslie precipitation are still relatively high. During 1983 the concentrations ranged between trace level up to a high of 1.7 ug/L and it does not seem to bear any relation with PCB amounts detected at Kejimkujik during the corresponding period. By excluding the value (1.7 ug/L), a mean of 0.17 ug/L is obtained from the positive values which is comparable to previous years' data. The fingerprint of this PCB trace positively matched that of Arochlor 1254, a commonly used PCB. This further substantiates the premise that local contamination is the responsible source. Potential sources could be burning wastes in landfills, industrial or small scale incinerators or even perhaps contaminated utility power transformers.

The annual mean concentrations for α-BHC and Lindane between the two sites were similar. The α-BHC means were also extremely close to the mean value (0.0172 ug/L) reported for the CANSOC Network (6) site at Truro, N.S. during the period between 1977-1981. The concentrations were somewhat lower than those from Gander with a mean of 0.0286 ug/L. The γ-BHC concentrations were also comparable thus indicating a persistence trend. However, the ratio of means for α-BHC to γ-BHC

isomers significantly decreased from 7.6 to 3.7 and from 5.6 to 2.6 for Kejimkujik Park and Ellerslie, respectively, when compared to 1982 data. The 1983 ratios coincided closely with the 1980-81 ratios and it is not known why relatively higher concentrations of α-BHC would be present in precipitation during 1982. Other pesticides were also observed sporadicly in samples but only at trace concentrations. Interestingly traces of chlordane and endosulfan isomers, heptachlor epoxide and dieldrin were detected for the first time in this study. These pesticides were previously reported present in CANSOC network (6) samples, however at very low concentrations and for a very low percentage of samples analyzed from the Atlantic Region.

All chlorobenzenes with the exception of 1,2,4,5 TeCB and hexachlorobenzene were encountered occasionally at concentrations generally low across the group except a few anomalously high values among the dichloro-isomers. This data should be interpreted with caution because of past problems generated by contaminated laboratory air and apparent sample contamination.

Polyaromatic hydrocarbons are formed by the high temperature pyrolysis of hydrocarbons or by the incomplete combustion of fossil fuels. An obvious emission pathway is thus through the atmosphere by which PAH's adhered to particulates or in the aerosol form are transported away from their emitting source. Data for PAH's in wet precipitation is very scarce and comparison is at this time not possible. All six PAH's were observed at least once in the twenty-four samples analyzed. The least prominent was B(g,h,i)Py present at only trace level in one sample. Conversely, fluoranthene which has the lowest

molecular weight of the six compounds and thus comparatively more volatile and water soluble was determined in the majority of samples. The annual mean concentration of 0.0076 ug/L for Kejimkujik Park samples represents only a minor decrease from previous years, whereas the annual mean of 0.014 ug/L for Ellerslie may indicate an increasing trend.

The December sample from Ellerslie contained higher than normal concentrations of PAH's and was excluded for this reason from the calculation of the means. A plausible explanation might be the scrubbing out effect of atmospheric contaminant during the initial part of a rain or snow event. This would result in a relatively concentrated sample when the sample volume is small. It should be noted that none of the samples were confirmed by gas chromatography/mass spectral analysis due to the very low concentrations observed and shortage of sample extract after G.C. and HPLC analyses.

In conclusion, results on precipitation samples collected during 1983 do not show any significant deviation compared with those obtained between late 1980 and 1982. The principal contaminants observed, namely the BHC isomers, PCB's and Fluoranthene appear to be quite persistent. It is highly probable that other contaminants were present in precipitation but were not observed because of such limiting factors as inherent weaknesses in the sample collection methods or lack of sufficiently sensitive analytical methods. Atmospheric transport certainly appears to be an important mode by which certain organic contaminants are scattered throughout the environment. Other unsuspected chemicals bearing similar physical and chemical properties are probably being dispersed in very much the same way. At present there is still

very little known in this field and much more research and monitoring effort should be invested to address the situation.

REFERENCES

(1) Brun, G.L.; "Data Summary Report for Trace Organics in Precipitation for 1980-81; Kejimkujik Park, N.S. and Ellerslie, P.E.I."; Internal Report (1982).

(2) Brun, G.L.; "Data Summary Report for Trace Organic Contaminants in Precipitation collected at Kejimkujik National Park, N.S. and Ellerslie, P.E.I. during 1982"; IWD-AR-WQB-83-44.

(3) Brun, G.L.; "Determination of Chlorinated Benzenes in Water by Capillary Gas Chromatography"; Internal Report (1981).

(4) Brun, G.L.; "Determination of PAH in Water and Sediment by HPLC"; Internal Report (1980).

(5) "Analytical Methods Manual"; IWD-WQB (1981).

(6) Brooksbank, P.; "The Canadian Network for Sampling Organic Compounds in Precipitation"; Technical Bulletin No. 129, IWD-WQB (1983).

TABLE 1

NAQUADAT METHOD CODES AND LIMITS OF DETECTION(1) FOR ORGANOCHLORINE PESTICIDES, PCB's, POLYAROMATIC HYDROCARBONS AND CHLORINATED BENZENES IN WATER

Name of Compound	NAQUADAT No.	Limit of Detection (ug/L)
α-BHC	18075	0.001
Lindane	18070	0.001
Heptachlor	18040	0.001
Aldrin	18130	0.001
Heptachlor Epoxide	18045	0.001
γ-Chlordane	18065	0.005
α-Chlordane	18060	0.005
α-Endosulfan	18050	0.01
p,p'-DDE	18020	0.001
Dieldrin	18150	0.001
Endrin	18140	0.01
o,p'-DDT	18005	0.001
p,p'-DDD	18010	0.001
β-Endosulfan	18055	0.01
p,p'-DDT	18000	0.001
Mirex	18125	0.001
Arochlors-Total	18164	0.005
1,3-DCB	17820	0.02
1,4-DCB	17821	0.02
1,2-DCB	17822	0.02
1,3,5-TCB	17830	0.004
1,2,4-TCB	17831	0.004
1,2,3-TCB	17832	0.004
1,2,3,5-TeCB	17840	0.002
1,2,4,5-TeCB	17841	0.002
1,2,3,4-TeCB	17842	0.002
PeCB	17850	0.002
HCB	17812	0.002
Fluoranthene	18904	0.005
Benzo(b) Fluoranthene	18901	0.003
Benzo(k) Fluoranthene	18903	0.002
Benzo(a) Pyrene	18900	0.003
Benzo(g,h,i) Perylene	18902	0.006
Indeno(1,2,3,cd) Pyrene	18905	0.005

(1) The limits of detection are based on a sample volume of 1.0 L; because the volume of precipitation varies constantly the limits of detection will also vary accordingly.

TABLE 2(a)

ORGANOCHLORINE PESTICIDES AND PCB's IN KEJIMKUJIK PARK[1] PRECIPITATION DURING 1983

Lab. Sample No.	Period of Collection (month)	Composite Volume (mL)	α-BHC	Lindane	Heptachlor	Aldrin	Heptachlor Epoxide	γ-Chlordane	α-Chlordane	α-Endosulfan	p,p'-DDE	Dieldrin	Endrin	o,p'-DDT	p,p'-DDD	β-Endosulfan	p,p'-DDT	Mirex	Arochlor-Total
Z02920	Jan.	3600	.008	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.040
Z03176	Feb.	3450	.011	.001	-	-	TR	-	-	-	TR	-	-	-	-	-	-	-	-
300002	Mar.	6650	.009	.003	-	TR	-	-	-	-	-	-	-	-	-	-	-	-	.053
300254	Apr.	6000	.008	TR	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.010
300712	May	5750	.020	.006	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
301104	Jun.	1550	.023	.004	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
301385	Jul.	4100	.020	.005	-	-	-	-	-	TR	-	-	-	-	-	TR	-	-	TR
301655	Aug.	2260	.015	.004	-	-	-	-	-	TR	-	TR	-	-	-	-	-	-	-
301996	Sep.	4860	.032	.009	-	-	-	-	-	TR	-	TR	-	-	-	TR	-	-	TR
302560	Oct.	2920	.025	.006	-	-	-	-	-	-	-	-	-	-	-	-	-	-	TR
303178	Nov.	5500	.009	.0009	-	-	-	-	-	-	-	-	-	-	-	-	-	-	TR
303321	Dec.	5960	.007	IN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.003
$\bar{x}$ (n = No. of Positive Values)		4380	.016	.0043															.027

(1) NAQUADAT Station No. 33NS01ED0004; Concentrations expressed in ug/L units;
TR = Trace = Small peak representing concentration below the limit of detection
IN = Interference

TABLE 2(b)

CHLORINATED BENZENES AND POLYAROMATIC HYDROCARBONS IN KEJIMKUJIK PARK PRECIPITATION DURING 1983

Lab. Sample No.	Period of Collection (month)	Composite Volume (mL)	1,3-DCB	1,4-DCB	1,2-DCB	1,3,5-TCB	1,2,4-TCB	1,2,3-TCB	1,2,3,5-TeCB	1,2,4,5-TeCB	1,2,3,4-TeCB	PeCB	HCB	Fl	B(b)Fl	B(k)Fl	B(a)P	B(g,h,i)P	I(1,2,3,cd)P
202920	Jan.	3600	-	-	-	-	-	-	-	-	-	-	-	.004	.002	.001	TR	-	-
203176	Feb.	3450	.030	-	-	-	-	-	.011	-	-	.003	-	.014	.005	.001	.001	-	-
300002	Mar.	6650	-	-	-	-	.009	-	.021	-	-	.000	-	.006	.001	TR	-	-	TR
300254	Apr.	6000	-	-	-	-	-	-	-	-	-	-	-	.004	-	-	-	-	-
300712	May	5750	-	-	-	-	-	-	-	-	-	-	-	.006	-	-	-	-	-
301104	Jun.	1550	-	.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
301385	Jul.	4100	-	-	-	-	-	-	-	-	-	-	-	.007	-	-	-	-	-
301655	Aug.	2260	-	-	TR	-	-	TR	-	-	-	-	-	.007	.002	-	-	-	-
301996	Sep.	4860	-	-	.020	TR	-	TR	-	-	-	-	-	.005	.002	.001	-	-	-
302560	Oct.	2920	-	.055	.037	-	-	-	-	-	-	-	-	.009	-	-	-	-	-
303178	Nov.	5500	-	IN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
303321	Dec.	5960	-	IN	-	-	-	-	-	-	.001	-	-	.014	.003	.001	.001	-	.004
$\bar{x}$ (n = No. Positive Values)		4380												.0076	.0025	.0010	.0010		

TABLE 3(a)

ORGANOCHLORINE PESTICIDES AND PCB's IN ELLERSLIE-PEI[1] PRECIPITATION DURING 1983

Lab. Sample No.	Period of Collection (month)	Composite Volume (mL)	α-BHC	Lindane	Heptachlor	Aldrin	Heptachlor Epoxide	γ-Chlordane	α-Chlordane	α-Endosulfan	p,p'-DDE	Dieldrin	Endrin	o,p'-DDT	p,p'-DDD	β-Endosulfan	p,p'-DDT	Mirex	Arochlor-Total
202921	Jan.	1680	.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.7[2]
203177	Feb.	820	.010	TR	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.32
300077	Mar.	2500	.006	-	-	-	-	-	TR	-	-	-	-	-	-	-	-	-	.15
300243	Apr.	2020	.008	TR	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.17
300711	May	5350	.017	0.005	-	-	-	-	-	-	.001	-	-	-	-	-	-	-	.07
301113	Jun.	2850	.015	.008	-	-	-	-	-	-	-	-	-	-	-	-	-	-	TR
301369	Jul.	3650	.008	.004	-	-	-	-	-	TR	-	-	-	-	-	TR	-	-	TR
301660	Aug.	3480	.017	.003	-	-	-	-	-	TR	-	-	-	-	-	TR	-	-	.061
302115	Sep.	2500	.020	.007	-	-	-	-	-	TR	-	TR	-	-	-	TR	-	-	TR
302559	Oct.	1930	.024	.008	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.13
303102	Nov.	5840	.025	.005	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.15
303322	Dec.	990	.013	IN	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.27
$\bar{x}$ (n = No. of Positive Values)		2800	.015	.0057															.17[3]

(1) NAQUADAT Station No. 33PE01CA0001; Concentration in ug/L units
TR = Trace = Small peak representing concentration below the limit of detection
IN = Interference
(2) Pattern of peaks matched that of Arochlor 1254
(3) Value for the Jan. sample excluded

TABLE 3(b)

CHLORINATED BENZENES AND POLYAROMATIC HYDROCARBONS IN ELLERSLIE-PEI PRECIPITATION DURING 1983

Lab. Sample No.	Period of Collection (month)	Composite Volume (mL)	1,3-DCB	1,4-DCB	1,2-DCB	1,3,5-TCB	1,2,4-TCB	1,2,3-TCB	1,2,3,5-TeCB	1,2,4,5-TeCB	1,2,3,4-TeCB	PeCB	HCB	Fl	B(b)Fl	B(k)Fl	B(a)P	B(g,h,i)Pe	I(1,2,3,cd)P
202921	Jan.	1680	-	-	-	-	-	-	-	-	-	-	-	.017	.014	.005	.005	-	-
203177	Feb.	820	-	-	-	-	-	-	-	-	-	.003	-	.047	.012	.005	TR	-	-
300077	Mar.	2500	-	-	-	-	-	-	.010	-	-	-	-	.008	-	-	-	-	-
300243	Apr.	2020	-	-	-	-	-	-	-	-	-	-	-	.009	-	-	-	-	-
300711	May	5350	-	.040	.03	-	-	-	-	-	-	-	-	.006	.001	TR	.001	-	.004
301113	Jun.	2850	-	.070	-	-	-	.008	-	-	-	-	-	.005	-	-	-	-	-
301369	Jul.	3650	-	-	-	TR	-	-	-	-	-	-	-	.007	-	-	-	-	-
301660	Aug.	3480	-	-	.02	TR	-	TR	-	-	-	-	-	.014	.003	.002	.003	-	-
302115	Sep.	2500	-	-	-	TR	-	-	-	-	-	-	-	.006	.001	.001	.001	-	-
302559	Oct.	1930	064	-	-	-	-	-	-	-	-	-	-	.014	.005	.002	.002	-	-
303102	Nov.	5840	-	IN	.035	.010	-	-	-	-	.002	-	-	.016	.004	.003	.004	TR	.006
303322	Dec.	990	-	IN	-	-	-	-	-	-	.006	-	-	.12	.023	.014	.010	-	.024
$\bar{x}$ (n = No. Positive Values)		2800												(4) .014	(4) .005	(4) .003	(4) .002		

(4) Value for Dec. Sample Excluded